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Emerging contaminants and nutrients in a saline aquifer of a complex environment☆

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A B S T R A C T

The quality and availability of water has become a pressing issue worldwide, being particularly important in semi-arid regions, where climate change has aggravated the problem. The use of anthropogenic chemicals, classified as emerging pollutants, adds to the problem representing a treat, since they are not regulated and have a potential impact on human and environmental health. This pressing problem has not been studied widely in complex environments like the one we present here. Distribution and seasonal variability of fecal sterols, alkylphenols, pesticides (emerging pollutants) and nutrients were determined in 35 wells used for agriculture and human consumption in the Valley of Maneadero, located in the semi-arid region of Baja California, Mexico. The presence of the tested pollutants in the saline aquifer was heterogeneous, showing important differences in concentration and distribution. Wells destined for household use showed the highest variability. In these wells, anthropogenic fecal sterols were detected and, alkylphenols, such as octyphenol and nonylphenol had maximum concentrations (2.7 ng/mL). In agriculture and urban wells, we identified DDT and organochlorine pesticides, as well as myclobutanil, which is considered a modern pesticide. Nitrates were identified in concentrations above international standards, mainly during the dry season, in both the agricultural and urban areas. As emerging pollutants represent a negative effect on environmental and human health, this is the first paper showing the importance of measuring this type of pollutant in agricultural/semi-urban areas, especially in aquifers that have been overexploited and communities that have relied on the use of septic tanks for decades.

1. Introduction

As the world's population increases, the challenges of supplying clean water for human consumption rise in every country highlighting the importance of monitoring the quality and quantity of the resource in order to guarantee sustainable consumption. Water pollution due to residual water from daily human activity leads to the contamination of groundwater and negative impacts on environmental and human health (Hench et al., 2003; Nelson et al., 2004; Foley et al., 2005; Wu et al., 2016).

Besides legacy contaminants, other emerging contaminants can also be found in wastewater. These emerging contaminants are typically unregulated chemical substances, and are suspected to affect the environment (Daughton, 2004). However, these emerging contaminants are recognized as potential pollutants for their adverse effects on the environment and human health. Among these emerging contaminants that have not been considered are: fecal sterols recognized as indicators of fecal contamination (Leeming et al., 1996; Mudge and Duce, 2005), and alkylphenols (nonylphenol, octyphenol, etc.) known as endocrine disruptors, neither of which is regulated (Barrios-Estrada et al., 2018). Although, both are persistent in the environment (Kelly, 1995; Lee et al., 2018).

For decades, the use of biological indicators that are able to

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distinguish between various sources of fecal pollution has been proposed (Leeming and Nichols, 1996; Sinton et al., 1998; Bull et al., 2002; Lyons et al., 2015), and is considered complementary or supplementary to traditional bacterial counts. One of the steroidal chemical indicators proposed as a fecal contamination indicator is coprostanol. It is the main element among neutral sterols found in animal feces and remains unaltered in water after treatments such as chlorination (Murtaugh and Bunch, 1967; Kirchmer, 1971; Leeming et al., 1996; Leeming and Nichols, 1996; Sinton et al., 1998; Bull et al., 2002; Cabral et al., 2018). Previous studies have shown that coprostanol concentrations correlate with coliform bacteria counts, particularly in environments contaminated with wastewater (Leeming and Nichols, 1996; Isobe et al., 2002). This makes coprostanol an ideal indicator for tracing human pollution in various environmental systems (O'Rourke, 1980; Writer et al., 1995; Mudge and Seguel, 1999; Carreira et al., 2004; Peng et al., 2005; Reeves and Patton, 2005; Ayebo et al., 2006; Field and Samadpour, 2007).

Among the most widely used indicators of fecal contamination is the ratio of coprostanol to cholesterol, which enables an evaluation of the degree of pollution of residual water (Leeming and Nichols, 1996; Isobe et al., 2002; Cabral and Martins, 2018). Cholesterol is a useful indicator of fecal pollution due to its ubiquitous nature and its origin from ingested plant material (Murtaugh and Bunch, 1967; Furtula et al., 2012). Sterol ratios commonly used include: a) [coprostanol/(coprostanol +β-cholestanol)], which identifies whether the sterol source is biogenic or residual water (Grimalt et al., 1990); b) coprostanol/epicoprostanol, which discerns between human and non-human pollution (Reeves and Patton, 2005); c) coprostanol/cholestanol, which differentiates between human and algal sterols (Nash et al., 2005; Devane et al., 2015); and d) coprostanol/cholesterol, which distinguishes between biogenic sources (Reeves and Patton, 2001; Peng et al., 2005).

Another pollutant in domestic residual water is alkylphenol, a type of surfactant widely used as part of industrial and household detergents and in pesticides for agriculture and various industrial products. Alkylphenols are used as alkylphenol ethoxylate, an alkylphenol with an ethoxy sidechain (Céspedes et al., 2008). Human exposure to alkylphenols occurs mainly through drinking water, eating contaminated food (Chrostowski, 2002), or during manufacturing (Luo et al., 2015; Liu et al., 2016). These chemical compounds have attracted the attention of scientists and environmentalists (Robles-Molina et al., 2014; Deyerling et al., 2016; Spindola-Vilela et al., 2018) since this type of compound interferes with the endocrine systems and bioaccumulates in aquatic organisms (Geyer et al., 2000; Spindola-Vilela et al., 2018). The main sources of water contamination include direct discharge of leachates, direct use of pesticides (Ying et al., 2002), and industrial and domestic water treatment plants (Pryor et al., 2002; Harrison et al., 2006; Stuart et al., 2012; Liao and Kannan, 2014; Gavrilescu et al., 2015).

Some pesticides are recognized as emerging contaminants (Murray et al., 2010; Barrios-Estrada et al., 2018) and are chemical mixtures designed to avoid, repel and kill pests, including herbicides, insecticides, fungicides, nematicides and acaricides. They can be classified according to their physicochemical characteristics, composition, or environmental half-life as organochlorines, organophosphates, carbamates, and triazines among others. Baja California is considered to be one of the 13 states in Mexico with the highest pesticide use. It is estimated that 80% of the total pesticide used in the country is used in Baja California (Camarena-Ojinaga et al., 2012). Despite the presence of these products in Mexicali Valley, little research has been conducted on their effects on public health and the environment (Moreno and López, 2005).

Water demand in Northwest Mexico, specifically in the city of Ensenada, has risen significantly over the past few decades. The population of Ensenada was estimated to be 519,813 in 2015, and is expected to reach over 623,000 by 2030 (CONAPO-SEGOB, 2014). Because of this growth trend tendency and the accompanying economical and industrial activities, as well as the development of the city in general, there is an increase in water demand. This demand is exacerbated by the decline in precipitation due to climate change and the scarcity of surface water. This work evaluated the presence and seasonal variations of emerging contaminants (fecal sterols, alkylphenols, pesticides) and nutrients in water wells used for agriculture and human consumption. The evaluated wells are part of an agricultural semi-urban environment from a saline and overexploited aquifer with human settlements that have used septic tanks for more than five decades. In this complex environment, little is known about these emerging contaminants.

1.1. Area of study

The Valley of Maneadero (VM) is located northwest of Baja California, Mexico, between 116° 30′ and 116° 40′ W, and between 31° 41′ and 31° 51' N, within the Ensenada municipality. The most important population settlement within the valley is the town Rodolfo Sánchez Taboada (commonly known as Maneadero), located in the east at the foothills of the Juarez mountain range. VM exhibits a homogenous topography with elevations between 0 and 20 m over sea level, while Maneadero town sits at a higher elevation between 40 and 80 m above sea level, surrounding the valley. The city of Ensenada lies approximately 10 km north of the town.

The Maneadero basin is adjacent to Ensenada, Real del Castillo and Ojos Negros basins to the North; the San Vicente and Laguna Salada basins to the East; the Santo Tomas basin to the South; and the Punta Banda Lagoon and Todos Santos Bay to the West (López-Fernández, 2009) (see Fig. 1).

In the site, in the last 70 years, the mean annual precipitation was 250 mm with a great inter-annual variability. Some years, rain could be over 200% from the annual mean and in the dry season it could only reach 30% of the annual mean (Huaico-Malhue, 2014). During the study, rain was 194 mm, which was 77.6% of the annual mean. In Mexico, the annual mean precipitation is 777 mm. Therefore; this zone is classified as semi-arid with rains in winter (November-April) and a dry season from May to October. The main temperatures in the zone are 12.5–15 °C in winter and 15–25 °C in summer, the zone's climate is Mediterranean (Méndez-González et al., 2008).

According to Licona-García (2011), groundwater in Maneadero is mainly used for agriculture, with 67% used for said purpose, 29% allocated for public-urban use, and the remaining 4% used for industrial activities (Luján-Flores, 2006; Huaico-Malhue, 2014). Maneadero has a 6700 ha unconfined aquifer, recharged with water coming from the San Carlos (862.5 km^2; 12.5 Mm^3) and Las Ánimas (1020.5 km^2; 20.8 Mm^3) streams. The streams are intermittent and only provide water to the aquifer during the wet season, while remaining dry the rest of the year (Mares-Olmos, 1996; Sarmiento-López, 1996; Huaico-Malhue, 2014). Within the area of the aquifer there are 321 active wells with depths lower than 40 m, as determined by the Ensenada Municipal Research and Planning Institute (IMIP, 2009; Lara-Valenzuela, 2011). This aquifer is considered the most important in the region since it provides 38% of potable water for the city of Ensenada and the town of Rodolfo Sánchez Taboada. The Maneadero aquifer has been overexploited since 1968 (Daesslé et al., 2005). Electromagnetic and geochemical analyses have indirectly shown that dissolved salts in groundwater have increased. In 2001–2002, concentrations of TDS oscillated between 540 and 9460 mg/L (Daesslé et al., 2005). In 2005–2006, according

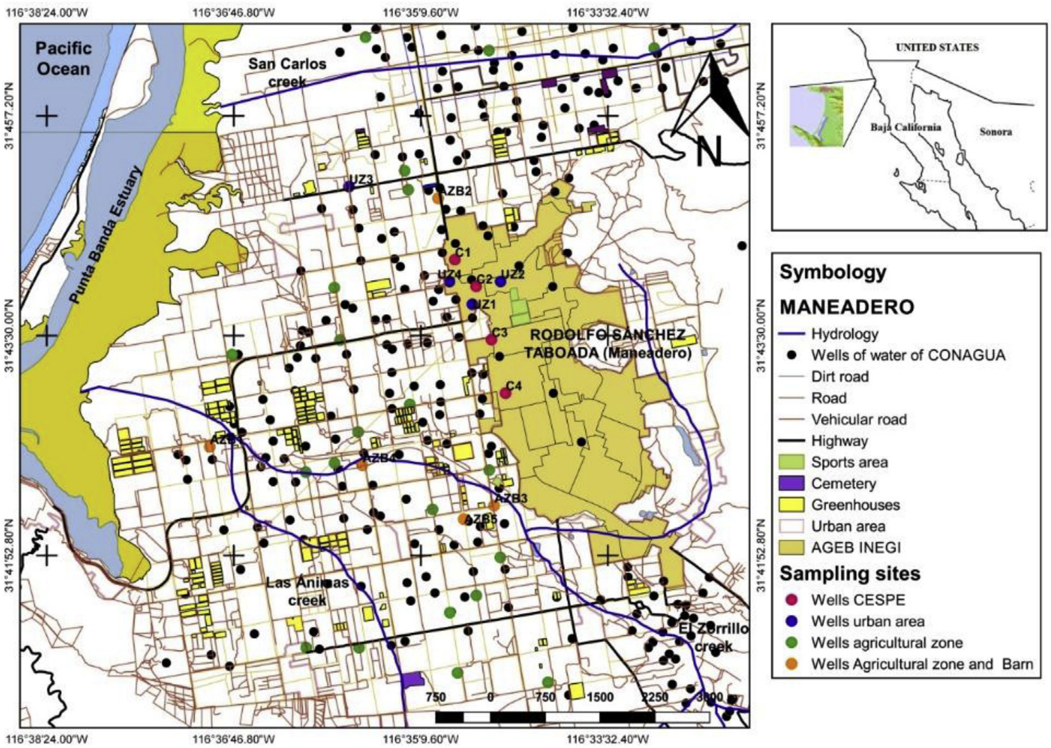

Fig. 1. Map of location of sampled wells.

to resistivity models assuming porosities and constant coefficients of cementing and textures, applying Archie's law, the calculated values for water salinity were between 1000 and 30,000 mg/L (Luján-Flores, 2006).

The States Office of Sustainable Rural Development Information of Baja California estimated Maneadero Valley's population at 22,957 in 2010 (INEGI, 2010). According to marginalization index reports about basic services per locality, the local sewerage system became operational in 2009 with 5799 households connected and 1560 not connected to the system. Water discharged through the system is treated at the El Salitral water treatment plant, estimating four users per sewage connection. This means that the treatment plant handles the sewage from roughly 16,950 people. An estimated total of 6240 residents discharge water residues in septic tanks (CONAPO, 2010). Agriculture in VM started at the end of the 19th century, which is around the time when septic tanks where first used. Having no sanitary hydraulic infrastructure could lead to the contamination of the aquifer's water and infiltration of pathogenic contaminants, presenting a potential health and environmental risk.

In this work, we analyzed faecal sterols and their relation to nutrient, pesticide and alkylphenol concentrations in wells used for drinking or field irrigation. This study was carried out in VM because it represents a complex environmental system, since it has historically been an agricultural zone where pesticides have been used indiscriminately. Furthermore, it has an unconfined aquifer that has been overexploited for 50 years with increasing salt concentrations, located in a semi-arid and semi-urban zone.

2. Methods

2.1. Sampling

Wells were selected based on the land use (i.e. agriculture, urban, etc.) and accessibility; water sampling from the wells was carried out twice a year, once during the dry season (September 2015) and once after the rainy season (March 2016). During both seasons, eight wells were sampled within the domestic-use area, four of the wells controlled by the State Public Services Commission of Ensenada (CESPE in Spanish) (C1-C4), and the remaining four from urban zones within the VM (UZ1-UZ4). In the agricultural-use area, 27 wells were sampled, 22 of which are for agricultural use only (AZ1-AZ22) and five are in areas with barns (AZB1-AZB5).

Samples were collected by switching on the well pump and letting it run for approximately 5 min. Collection bottles were washed with water from the well and filled to the rim when samples were used for nutrient measurement. For other analyses, bottles were only half filled. Each sample was geotagged at the sampling site and kept on ice until tested. Nitrates, nitrites and phosphates were tested in sterile 50 mL plastic tubes no later than 6 h after sampling. Fecal sterols, pesticides and alkylphenols were tested in clean 250 mL amber glass bottles, covered with aluminum foil, placed on ice for transport, and later frozen at −20 °C until testing at the Geothermal Fluid Advanced Geochemistry Unit, part of the Mexican Geothermal Energy Innovation Center (CeMIE-Geo).

2.2. Tests

Oxide-reduction potential (Eh), hydrogen potential (pH), electrical conductivity and total dissolved solids (TDS) were tested on-site using a Hach MP-6p multiparameter. For nitrate and phosphate tests, water samples were filtered using a 45 μm cellulose filter and the sample was fractionated in three aliquots of 10 mL. Specific test reagent mixtures (Hach powder pillows: Nitraver5, Nitriver3, Phosver3) were added according to the manufacturer's instructions and estimations were carried out colorimetrically using a Hach DR900 colorimeter.

2.3. Analyses

2.3.1. Alkylphenols and pesticides

Alkylphenols and pesticides were measured with GC-MS using an Agilent 7890B gas chromatographer coupled to an Agilent 7000C triple quadrupole mass spectrometer with electron ionization. Helium (99.99% pure) was used as a carrying agent at a constant flow of 0.9 mL/min. All organic solvents used were HPLC grade. Briefly, samples were incubated for 1 min at 75 °C, before the temperature was increased to 175 °C with a 25 °C/min ramp rate, then to 250 °C with a 4 °C/min ramp rate. Finally, the temperature was increased to 300 °C with a 25 °C/min ramp rate and kept for 10 min. To separate the compounds of interest, micro extraction in the solid phase was used with a mixture of recovery patterns (bisphenol A-D16; 2, 4, 5, 6-tetrachloro-m-xylene; biphenyl polychlorinated (PCB) 209). Subsequently, samples were micro extracted with polydimethylsiloxane (PDMS) fiber in direct immersion mode.

For pesticide quantification, calibration curves were prepared with concentrations from 0.01 to 200 ng/L, obtaining r^2 values between 0.895 and 0.995. For alkylphenol quantification, calibration curves were prepared using concentrations ranging from 0.10 to 2000 ng/L, obtaining r^2 values of between 0.883 and 0.992. Before loading samples, trial runs were carried out with respective standards at 20 ng/L concentrations, getting recoveries between 82 and 106%.

Detection limits expressed in ng/L, for each compound were as follows: 0.038 for 4-tert-octyphenol, 0.106 for nonylphenol (technical mixture), 0.229 for octyphenol ethoxylates, 0.321 for nonylphenol ethoxylates (technical mixture), 0.897 for nonylphenol diethoxylates (technical mixture), 0.004 for α-hexachlorocyclohexane, 0.004 for ß-hexachlorocyclohexane, 0.002 for γ-hexachlorocyclohexane (lindane), 0.004 for δ-hexachlorocyclohexane, 0.001 for heptachlor, 0.003 for heptachlor epoxy B, 0.016 for α-endosulfan, 0.027 for ß-endosulfan, 0.061 for endosulfan sulphate, 0.001 for 4,4′-DDE, 0.262 for 4,4′-DDD, 0.139 for 4,4′-DDT, 1.386 for endrin, 0.568 for dieldrin, and 0.583 for myclobutanil.

2.3.2. Faecal sterols

Faecal sterols were measured using the same setup as the one used for alkylphenols and pesticides. Solid phase extraction of faecal sterols was adapted from Jeanneau et al. (2011), using ENVI™-18 DSK SPE Disc (47 mm diameter). The discs were washed with dichloromethane (DCM) and conditioned with MeOH. After this procedure, discs were sequentially eluted by gravity, and then the sample was poured and under vacuum, eluted through the disc. Once the discs were dry, they were stored for 24 h at 4 °C in 50 mL of DCM to recover the extracted analytes. After this time, samples were shaken in a Vortex shaker (1000 rpm × 2 min). The DCM was transferred to amber vials of 40 mL, where it was evaporated using nitrogen flow (99.998% purity) until a volume of approximately 1 mL was obtained. The extracts were passed through columns of Na_2SO_4 to remove any trace of water. Finally, these extracts were evaporated to dryness with a smooth flow of nitrogen. On the same day of chromatographic analysis, 50 μL of derivatization reagent BSTFA and 10 μL of pyridine were added to each vial. To perform the derivatization reaction, vials were heated at 70 °C for 30 min. Finally, once cooled to room temperature, the volume was adjusted to 200 μL with iso-octane (Flores-Lugo, 2016).

Calibration curves were calculated using iso-octane-diluted standards at concentrations ranging from 0.005 to 100 ng/mL, with r^2 values from 0.992 to 0.999. Trial runs were performed using standards at 100 ng/mL, obtaining recoveries of between 82 and 114%. Detection limits expressed in ng/L for each compound were 8.21 for coprostanol, 0.59 for epi-coprostanol, 0.21 for epi-cholestanol, 0.023 for cholesterol, 0.19 for β-cholestanol, 1.23 for campesterol, 0.65 for stigmasterol, and 3.19 for β-sitostanol.

3. Results and discussion

3.1. Hydrogen potential (pH) and redox potential (Eh)

During both sampling seasons, 90% of samples exhibited pH values ranging from 6.88 to 7.52 (SM 1a). This is within permissible values established by current regulations for agriculture and livestock use, and for flora and fauna preservation (Aher, 2012). Our pH values show seasonal variability among samples, which may be a result of dissolved gases and solids (Patil and Nagarajan, 2015). However, pH values remain within a small range of change.

According to the oxidation/reduction potential (Eh) measured in samples, it was considerably higher in the four CESPE-administered wells, with a range between 400 and 700 mV, in comparison with the rest of the studied wells (−40 to 200 mV) (SM 1b). Eh allows us to infer the distribution of certain mineral species along the aquifer (Husson, 2013), it also impacts on the distribution and metabolic activity of microorganisms (Pedersen and Ekendahl, 1990). Despite Eh being an important indicator of the mobility of various metals and chemicals sensitive to oxidative and reductive conditions, to our knowledge, Eh has not been previously studied in VM.

Looking at chemical species charts for fresh water within the range of pH (6.9–7.7) and Eh (400–700 mV) values in drinking wells (CESPE-administrated), metal species of Ba, Ca, Cd, Cu, Na and Ni would be in the solution as dissolved anions. In the case of other chemical elements of environmental concern, Co, Cr, Hg, U and Pb may be present as hydroxides. Both groups of elements are mobile in water and free to form compounds with any available anion as Cl^-, HCO_3, HPO_4^{2-}, SO_4^{2-}, etc. In this case, based on the formed compound and concentration, there will be an associated toxicological risk (Geological Survey of Japan, 2005). On the other hand, metalloids such as As, Sb or Se (no metal) may occur as arsenate ($HAsO_4^{2-}$) that is mobile but less toxic than arsenite. Antimony could be precipitated as $SbO_4(s)$ or $Sb_2O_5(s)$. Selenium could be present as selenite hydrogen ion ($HSeO_3^-$), selenite (SeO_3^{2-}) or selenate ion (SeO_4^{2-}), this could represent a health threat, since selenite is more toxic (Goldberg et al., 2006) at higher concentrations than 0.01 mg/L in drinking water (Gordon et al., 2008).

3.2. Electrical conductivity (EC) and total dissolved solids (TDS)

In our results, seasonal variations in EC and TDS values in all samples were not significant (SM 3c, 3d). The minimal EC values measured during our study were 0.918 mS/cm during the dry season and 0.753 mS/cm post-rains. Maximum EC values during the dry season were 27.2 mS/cm, whereas during the post-rains season maximum values were 27.12 mS/cm, with average values of 6.64 mS/cm (SM 1c). Our results also show that EC values are above those recommended for agricultural use (Ayers and Westcot, 1976), unless it is used for salt-tolerant crops, although soil will eventually be affected.

Our results show that, during both seasons, water used for irrigation had TDS levels between 516 and 26,730 mg/L, in contrast, the range of wells used for human consumption was between 2400 and 5965 mg/L. When compared with previous studies in the area that reported values between 540 and 8550 mg/L, we observed that TDS increased three-fold over a ten year period, (Sánchez-Rentería, 2004). Total dissolved solids (TDS) (SM 1d) are a measure of the total amount of organic and inorganic substances suspended in a liquid as molecules, ions or micro-granules (Balal et al., 2015). TDS from natural water sources ranges from 30 to 6000 mg/L (WHO/

UNEP, 1989), however, values lower than 1000 mg/L are recommended for human consumption in Mexico (DOF, 1994).

High levels of TDS during the sampling period could be related to the composition of the particulate matter that is characteristic of this kind of environment (Dimari et al., 2008). This particulate matter is commonly composed of organic and inorganic chemicals and microbial communities (Kaufman et al., 2005; Xanes et al., 2006). Salgado-Tránsito et al. (2012) determined the effect of water quality on the Guadalupe Valley aquifer (located 36 km NE from VM). They measured pH, EC, TDS and the concentration of main ions in the water of 66 wells. They found that water salinity is not present in the total area of Guadalupe Valley, so the water in the aquifer is not the only cause of the problem. They suggested careful management of the water for irrigation and excessive application of fertilizers that contribute to the salinity.

The observed EC and TDS values in VM are mainly attributed to seawater intrusion (Pérez-Flores et al., 2004), although isotope analyses for $^{87}Sr/^{86}Sr$, δ^2H and $\delta^{18}O$ suggest different possible sources for the elevated salinity. The salts recycling process (evaporation, soil accumulation and wash during rainy seasons), the dissolution of gypsum or anhydrite (elevated values of SO_4/Cl ratio), and the presence of deep sub aquifers with different chemical compositions (fossil waters of non-marine origin) are within these sources (Lara-Valenzuela, 2011).

If we consider that 494 wells are registered to pump water for use and human consumption in VM where the surface area is 75 km^2, we can expect important changes in the hydrodynamics of the aquifer. This phenomenon will alter the hydraulic gradient of the natural equilibrium between freshwater and seawater, reflected in changes in the hydrostatic pressure. These changes may lead to the infiltration of seawater and/or saline water from deeper aquifers to the freshwater aquifer.

High TDS concentrations can reduce water quality and affect hydric balance in single organism and aquatic life. Consuming water with TDS>1000 mg/L has been associated with an increased incidence of kidney stones (Panhwar et al., 2013). Previous studies have found an inverse relationship between TDS in drinking water and the incidence of certain types of cancer, and coronary and cardiovascular disease (Burton and Cornhill, 1977; Juranek and Mac Kenzie, 1998; Craun, 2018).

3.3. Nitrates, nitrites and phosphates

According to nitrates, nitrites and phosphates concentrations in groundwater during both sampling seasons (SM 2a, 2b and 2c), we observed that nitrate (NO_3-N) concentrations were the highest. This nutrient reached levels slightly higher than 100 mg/L, followed by phosphate concentrations, with a maximum of 2.2 mg/L, and nitrite concentrations, which reached up to 0.65 mg/L.

Nitrate concentrations were higher during the rainy reason than during dry season. Temporal variations were relatively small with lower concentrations during the post-rains season in the majority of wells; apart from three agricultural wells and three agricultural wells with barns, which can be attributed to dilution, as has been reported in similar studies (Nakagawa et al., 2016). Around 69% of wells exhibited concentrations above the allowed levels for drinking water. Moreover, this is the case for CESPE-administered wells, and three out of four urban wells, which had concentrations above permissible levels regardless of the season.

Nitrite concentrations were below the maximum levels (1 mg/L) established by the WHO (2011), with agricultural zone wells having the higher concentrations (up to 0.6 mg/L). For most of the wells tested, in dry season the concentrations were lower than in post rain season. In wells AZ14, AZ17, AZ19 and AZ20 during wet season, the concentrations were higher than during dry seasons. The differences can be attributed to local factors such as permeability changes, runoff, higher irrigation rates or subterranean water flow connections; on the surface, these wells are not apparently related (Fig. 1).

Nitrates in soil, surface water and groundwater are a result of decomposition of nitrogenized organic matter (Kreitler and Jones, 1975) and are related to farming activities and leakage of unrehabilitated sewage systems (El Alfy et al., 2017). Nitrites are a result of the conversion of nitrate to nitrite, which occurs under alkaline conditions where nitrate is reduced to nitrite and then to nitrogen gas. Therefore, nitrite sources in the environment are the same for nitrate (Cheng et al., 1997). Surface water generally contains nitrate concentrations lower than 10 mg/L, often lower than 1 mg/L, and rarely exceeding 3 mg/L. Nitrate is of particular interest since its consumption through water can be toxic in humans, particularly infants (Yang et al., 1998; Sadler et al., 2016). Consumption of nitrites with concentrations of 45 mg/L lead to Methemoglobinemia (Ayebo et al., 1997). The first reports of poisoning in the US due to nitrite consumption through water dates back to 1944 (Craun, 2018). Since then, the WHO (2011) has established a maximum permissible value of 10 mg/L for nitrates (NO_3-N) and 1 mg/L for nitrites in water intended for domestic use. Importantly, it is not customary for people in the Ensenada municipality to drink tap water (Daesslé et al., 2005; Daesslé, 2009; Daesslé et al., 2014; Espinosa-Fernández and Valencia-Hitte, 2017; Huaico-Malhue et al., 2017). Instead, they rely on bottled water produced locally using reverse osmosis, however, there is no data to show how many people drink tap water, and it is believed that most people use tap water for cooking (Maier, 2001).

Interestingly, despite phosphate being an important component of fertilizers, detergents and pesticides, most of the wells (except 5) had levels below 1 mg/L, the level established to avoid eutrophication problems (Zhao and Sengupta, 1998). These values were not expected since agriculture is the main activity of the VM and phosphate is a nutrient widely used as fertilizer. However, it has been reported that repeated applications of phosphorus as fertilizer in higher amounts than needed by plants in sandy soils, and the use of high volumes of irrigation water; can lead to a saturation of phosphorus at horizon A in soil by adsorption, maintaining the phosphorous in soil phase with a decline of its presence in groundwater (Hendricks et al., 2014). This phenomenon might be happening in VM, therefore, low phosphate concentrations were measured in water.

Values of pH and Eh, when compared to nitrogen and phosphorus chemical species charts for fresh water (Geological Survey of Japan, 2005) indicate that the chemical species that are most likely to be present in water are: N_2 (aq), NO_3^-, $H_2PO_4^{2-}$ and $H_2PO_4^-$.

3.4. Emerging pollutants

3.4.1. Alkylphenols

During the dry season CESPE-administered wells had higher alkylphenol concentrations, up to 2.27 ng/mL (SM 2d), which are particularly high in the central agricultural area (1.5 ng/mL). During the rainy season, the highest concentrations are found in the agricultural zone as well. However, there is a dilution effect in the central part of the valley, due to rains and the rapid recharge of the aquifer. In this study, we detected alkylphenols in both the urban and agricultural areas (C, UZ, AZ, and AZB) which evidence a generalized use of these types of compounds.

In CESPE-administered wells maximum concentrations were 2.27 ng/mL during the dry season, significantly higher than the 1 ng/mL nonylphenol concentrations recommended by the Canadian water quality guidelines for the protection of aquatic life (Minister of Health Canada, 2013). A previous study carried out in

Quebec, showed nonylphenol concentrations in drinking water up to 43.3 ng/mL, with a mean of 10.4 ng/mL (Berryman et al., 2004). The environmental protection agency of the USA has accepted the risks of nonylphenol and has prepared a guideline for ambient water quality, recommending nonylphenol concentrations in freshwater <6.6 μg/L and, in saltwater <1.7 μg/L (Brooke and Thursby, 2005). In the case of the European Union, a restriction was proposed in nonyphenol of nonylphenol etoxylates concentrations higher than 100 mg/kg, placed on the market of textile articles that can be washed in water. Likewise these chemicals shall not be placed on the market after February 3rd, 2021 in textile articles expected to be washed in water during their normal life-cycle (OJEU, 2016).

Several studies have shown phenolic compounds to be related to an increased risk of certain types of cancer and diabetes mellitus (Shankar and Teppala, 2011; Kim and Park, 2013), heart disease (Melzer et al., 2010; Shankar et al., 2012) and hypertension (Bae et al., 2012). They have also been associated with the deterioration of reproductive functions (Nimrod and Benson, 1996; Rogers et al., 2013; Massart et al., 2015; Wu et al., 2015), and are classified as endocrine disruptors (Priac et al., 2017). However, many countries, including China, India, Mexico and several South American countries use and produce nonylphenolic compounds in large quantities and no action has been taken by any of these countries to reduce or eliminate their usage (Soares et al., 2008).

3.4.2. Pesticides

In our study, we analyzed various types of pesticides and grouped them as follows: (a) emerging pesticides; (b) dichlorodiphenyltrichloroethane (DDT) and its derivatives; and (c) myclobutanil, considered a modern pesticide. Emerging pesticides were detected in all tested wells (N = 36), indicating that these pesticides have been used historically and continue to be used. As leachates from fields can reach underground aquifers, concentrations of these types of pesticides often exceed Mexican regulations (NOM, Mexican Official Norm) for potable and recreational water (Warnemuende and Kanwar, 2002).

Detected pesticides, arranged in descending order according to percentage of detection in sampled wells, are as follows: β -hexachlorocyclohexane (86%) > α-hexachlorocyclohexane (72%) > heptachlorine (50%) > endrin (45%) > 4,4′-DDD (34%) > δ-hexachlorocyclohexane (31%) > heptachlorine epoxide B (25%) > endosulfan sulphate (23%) > 4,4′-DDE (8.3%) > α-endosulfan (8%) > β-endosulfan (5.6%) > 4,4′-DDT (2.8%). Whereas for the post-rain season they were: β-hexachlorocyclohexane (42%) > α-hexachlorocyclohexane (39%) > heptachlorine (38%) > endrin (28%) > 4,4′-DDT (20%) > β-endosulfan (11%) > α-endosulfan, dieldrin and 4,4′-DDD (2.8%).

The Stockholm Convention (SC) on Persistent Organic Pollutants, of which Mexico is a signatory, sets a roadmap for the prohibition of compounds such as aldrin, dieldrin, endrin, heptachlorine, mirex, chlordane, toxaphene, hexahlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT) and its metabolites, dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD), α-hexachlorocyclohexane (α-HCH), γ-hexachlorocyclohexane (γ-HCH, lindane), endosulfan, methoxychlor and chlordecone (SEMARNAT, 2007; Romero-Torres et al., 2009). These pollutants reach groundwater, rivers, lakes and, finally, the ocean as sediments and chemical loads transported by rivers (Criswell, 1998), and have been detected in various parts of the world (Tan and Vijayaletchumy, 1994; Caldas et al., 1999; Konstantinou et al., 2006; Guzzella et al., 2011; Ellis et al., 2018), even in birds (Jiménez et al., 2005). A study of residential soils in the Mexicali Valley (located 262 km NE from the MV) showed that compared to the global regulatory guideline values, all hexachlorocyclohexanes and chlordanes measurements were below the mean values but above the lowest values in some cases; aged DDT was identified in most soils and technical HCH plus lindane (Sánchez-Osorio et al., 2017).

Regarding DDT and its derivatives, it is worth mentioning that these compounds were not detected in all wells. The highest detected concentration of 4,4‘-DDT in the Valley was 28.79 ng/L during the dry season in well AZ5. During the post-rain season, 4,4‘-DDT was detected in seven wells (C1, C4, AZ1, AZ3, AZ8, AZ12 and AZB3), with concentrations between 0.19 and 2.73 ng/L. During the dry season 4,4‘-DDT was detected in 12 wells (C1-4, UZ1, AZ1-3, AZ5, 6, AZB1, 2), with concentrations between 4.97 and 71.81 ng/L 4,4‘-DDE was detected in three wells with concentrations between 0.25 and 2.47 ng/L. During the post-rain season a single well (AZB3) had detectable concentrations of 4,4‘-DDD (0.85 ng/L) and none had detectable 4,4‘-DDE. The origin of DDT in water could also come from the soil or sediment, according to what has been reported in previous studies in an urbanized estuarine bay in China (Feng et al., 2016). Therefore, to determine its source, further research at this site should be performed.

In order to estimate the age of DDT contamination and its derivatives we employed the (DDD+DDE)/DDT relation (Zhang et al., 2002), where values > 1 represent older pollutants and values < 1 represent recent contamination. In our results, during rainy season four agricultural wells, one agricultural with barn and two CESPE-administrated wells presented values < 1, which represents a recent contamination in wells. For dry season, all wells presented evidence of older pollutants. The quotient <1, indicates that DDT is in higher concentrations than its metabolites DDE and DDD (Lal and Saxena, 1982). Comparing the quotient values obtained with DDT half-life in soil (SM 3), which is lower than 15 years (USDHHS, 2002), we infer that the detected residues correspond to DDT used within the last 15 years despite this chemical being prohibited since 1991 in Mexico (Gips, 1987; DOF, 1994).

Based on the calculated relation, 89.2% of dry season samples show values higher than 1, indicating elevated concentrations of DDE and DDD and suggesting that degradation of DDT in soil is more effective. In contrast, during the post-rain season, 10.8% of samples showed relation values lower than 1, indicating a lower rate of DDT degradation in soil (USDHHS, 2002; Chen et al., 2008; Uzcategui et al., 2011).

In our study, we detected myclobutanil concentrations between 0.050 and 0.519 ng/mL during the dry season and between 0.0077 and 0.216 ng/mL during the post-rain season. These values are considerably lower than the ones found during a previous study conducted in the Yarra basin in Australia that found maximum concentrations of myclobutanil of 2.9 ng/mL (Wightwick et al., 2012). Organochlorine compounds studied are found in the most commercially successful insecticides in Mexico, and are used in agriculture, households, gardening, and in industrial and commercial buildings. Of these, myclobutanil is one of the most persistent, having a half-life of 15 days in water, being moderately mobile and being able to leach into groundwater (Celeiro et al., 2017).

In general, pesticide concentrations vary between seasons, indicating that climate variations affect the concentration and distribution of contaminants. The emerging pesticides showed lower concentrations during the dry season in comparison to the rainy season where most of these compounds were distributed in the central part of VM. In the case of myclobutanil, higher concentrations were identified in the dry season mainly in the northern part of VM, close to CESPE-administrated wells and the central part. These results suggest a wide use of modern and emerging pesticides in the region.

3.4.3. Fecal sterols

Abundance of fecal sterols detected in sampled wells is shown in SM 4. Here we observe that the highest concentrations correspond to stigmasterol (94.43 ng/mL) and sitostanol (12.68 ng/mL), both of which are plant sterols characteristic of marine algae (Grimalt et al., 1990). Comparing our results with farming fields irrigated with wastewater in sandy soils, stigmasterol and sitostanol were found in 24 and 23 ng/mL (Biache et al., 2015). Therefore, our results further strengthen the theory of seawater infiltrating the aquifer. We also detected epicoprostanol, a coprostanol isomer found as a trace in large mammals (Martin et al., 1973), and used as a biomarker of human faeces.

Leeming and Nichols (1996) showed that fecal sterols are indicators of fecal contamination. The specific source of such contamination is based on three factors: 1) animal diet, which can vary between carnivores, herbivores and omnivores; 2) animal-synthesized sterols non-related to diet; and 3) stanol isomers resulting from bio-hydrogenation of sterols by anaerobic bacteria in the digestive tract. In order to discern between sources of fecal matter we calculated molecular ratios relating fecal sterols concentrations (R) (Table 1). This allowed us to identify human fecal contamination from untreated (R1) or partially treated (R2, R3) residual water. This is as well as differentiating it from fecal contamination from bovines (R5), ruminants (R6), and other sources of fecal contamination (R7).

Fig. 2 shows calculated values for R1-R6, for both sampling seasons, where we identified the source of fecal pollution in the VM. In general, the majority of wells presented to be moderately contaminated from residual waters and fecal sterols mainly from humans. It is of particular importance that CESPE-administered wells (C1-C4) were contaminated by fecal sterols, independently of the sampling season. We found higher levels of fecal sterol contaminations in CESPE-administered wells in the agricultural zone and the agricultural zone with barns (R1, R2 and R3). The ratio of epicoprostanol and coprostanol (R4), proposed by Mudge and Seguel (1999), is used as an indicator of the level of residual water-treatment, based on the fact that epicoprostanol is produced during the water-treatment process. Based on R4, results indicate that most of the water bodies received untreated or partially treated wastewater, originated by the inefficiency of the wastewater treatment systems currently operating in VM or the extensive use of septic tanks.

Differentiating between human and animal fecal contamination (R5 and R6), we found that fecal contamination in wells is of human origin, with one CESPE-administered well (C2) showing fecal contamination of ruminant source. Unexpectedly, in wells in the agricultural zone with barns, where animal-sourced fecal contamination was anticipated, we found a mix of human and animal-sourced fecal contamination, with some wells having a higher proportion of fecal contamination of human origin.

Values for R7 are summarized in Fig. 3. These maps were constructed from the application of the location-allocation models in vector format with the software Q-Gis 2.18, in a network that allows differentiation of factors that are interrelated by specific elements, with the information obtained, so that interpolations were continued through the weighted inverse distance method (IDW) for the preparation of thematic maps. Values < 0.3 represent non-contaminated areas, the majority of which are found during the post-rain season, mainly in northern VM. During this season, fecal contamination was heightened in the paths of the Ánimas and El Zorrillo streams. Contrary to this, most wells showed fecal contamination during the dry season, evidenced by R7 values > 0.7. We also observed that well C2, administered by CESPE, shows fecal contamination during both sampling seasons. The observed seasonal variation, despite low precipitation of 194 mm during our sampling period, is an indicator of variability in the area and evidence of how fast the aquifer responds to small changes in water levels.

Table 1
Equations of calculated molecular proportions for fecal sterols and their assessment criteria.

ID	Molecular Proportions	Threshold level	Criteria	References
R1	coprostanol/(coprostanol + cholestanol)	≥0.3	Moderate sewage contaminated	(Grimalt et al., 1990; Fattore et al., 1996; Patton and Reeves, 1999; Marvin et al., 2001; Bull et al., 2002; Carreira et al., 2004; Reeves and Patton, 2005; Martins et al., 2007; Cordeiro et al., 2008; Zhang et al., 2008; Froehner et al., 2009; Furtula et al., 2012; Matić Bujagić et al., 2016)
		≥0.7	Highly sewage contaminated	
R2	coprostanol/cholesterol	>0.2	Sewage contaminated	(Quéméneur and Marty, 1994; Fattore et al., 1996; Leeming and Nichols, 1996; Mudge and Seguel, 1999; Patton and Reeves, 1999; Carreira et al., 2004; Reeves and Patton, 2005; Cordeiro et al., 2008; Zhang et al., 2008; Alsalahi et al., 2015; Matić Bujagić et al., 2016)
		>1.0	Highly sewage contaminated	
R3	coprostanol/(cholestanol + cholesterol)	<0.06	Sewage contaminated	(Writer et al., 1995; Jeanneau et al., 2011; Gottschall et al., 2013; Lim et al., 2017)
		>0.06	Highly sewage contaminated	
R4	epicoprostanol/coprostanol	<0.2	Human fecal contaminated	(Mudge and Seguel, 1999; Martins et al., 2007; Froehner et al., 2009; Adnan et al., 2012; Furtula et al., 2012; Matić Bujagić et al., 2016)
		>0.8	uncontaminated	
R5	sitostanol/coprostanol	<1.0	Human or porcine feces contaminated	(Gourmelon et al., 2010; Jeanneau et al., 2011)
		>1.0	Bobine manure contaminated	
R6	epicoprostanol/(coprostanol + cholesterol)	<1.5	Human feces contaminated	(Bethell et al., 1994; Bull et al., 2002)
		>1.5	Rumiant contaminated	
R7	(coprostanol+epicoprostanol)/(coprostanol,+epicoprostanol+cholestenol)	<0.3	uncontaminated	(Bull et al., 1999, 2002; Reeves and Patton, 2005; Shillito et al., 2011; Furtula et al., 2012; Lim et al., 2017; Prost et al., 2017)
		>0.7	contaminated	

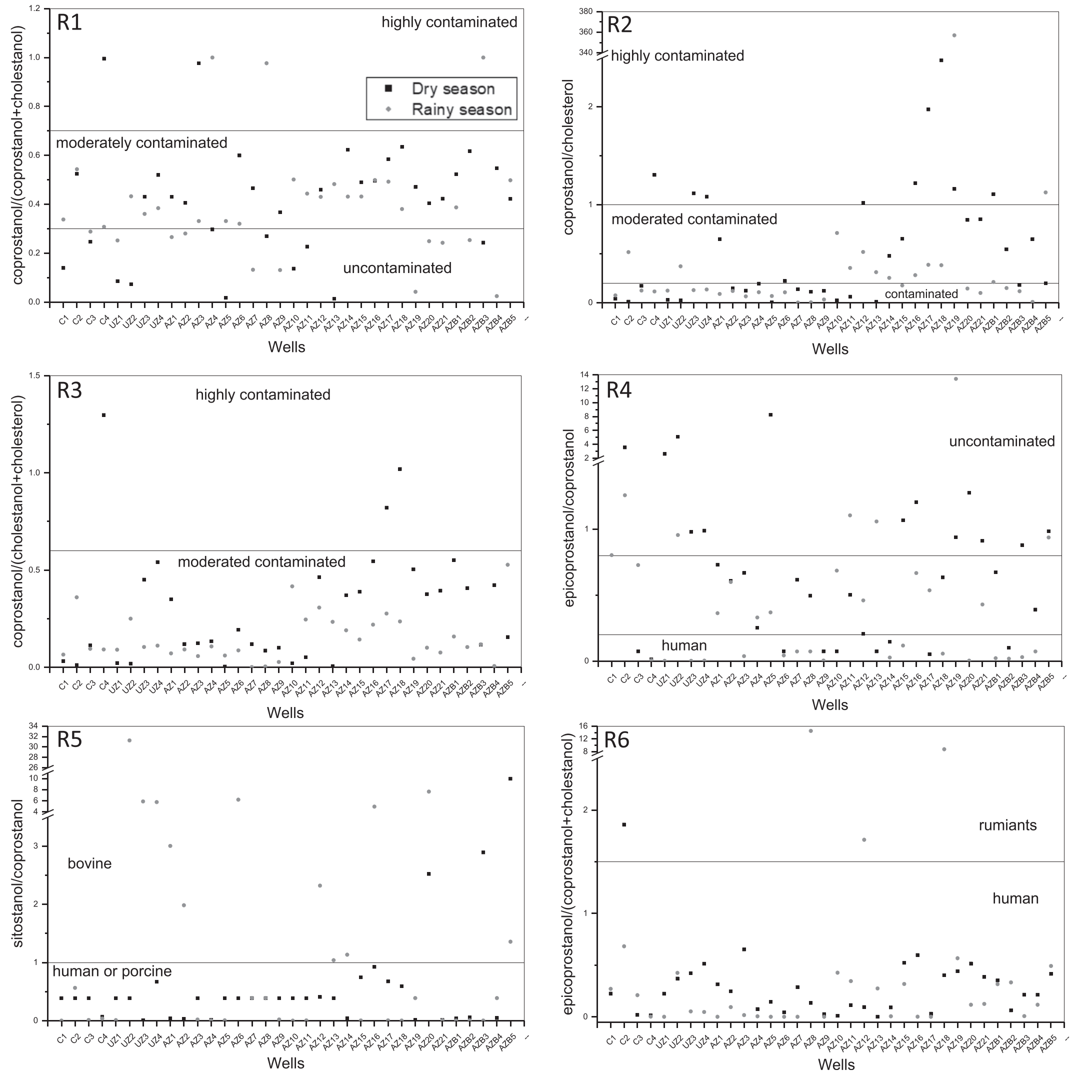

Fig. 2. a) R1, b) R2, c) R3, d) R4, e) R5, f) R6. Where: C1-C4 are wells administrated by CESPE, UZ – wells from urban zone; AZ – wells from agricultural zone; AZB – wells from agricultural zone with barn. Horizontal lines represent the ranges mentioned in table 1.

4. Conclusions

Emerging pollutants detected in groundwater samples include a wide range of anthropogenic substances, which have dispersed widely and are present in well water. Among the identified factors promoting the above, is the use of pesticides, including DDT, despite being prohibited for years. The use of detergents and their presence as alkylphenols are recognized as renal disruptors.

The excessive use of fertilizers is reflected in high nitrate concentrations. In addition, off course, the use of septic tanks for over 50 years has manifested with the presence of fecal sterols, mainly of human origin. There is a possibility of the bay being an additional source of fecal sterols by marine intrusion, strengthened by the detection of stigmasterol, which originates from marine algae.

Regarding CESPE-administered wells (C1-C4), taking into account that these wells are for human consumption and can represent a potential health risk, we recommend frequent vigilance with the contaminants evaluated in this study.

An important variation was observed in concentration and distribution of all chemicals tested, showing a fast response of the aquifer in respect to the rain. Consequently, before thinking about an artificial recharge of the aquifer with treated wastewater, a response to the lack of water in the city is required. It is convenient to conduct studies in pilot tests measuring emerging and legacy pollutants. In the case of fecal sterols, it is necessary to evaluate their contribution to eco-toxicological risk to predict what effects they may have on public health and the environment.

Bearing in mind that water is the main resource for the development of agriculture, livestock and human activities in the area, a calendar for continuous monitoring should be prepared since there are no inventories. As well as a water resource management, planning to understand the behavior origin and change of emerging pollutants in sub-urban agricultural basins is required. This will guarantee the quality of the water used for irrigation and human consumption in this complex environment.

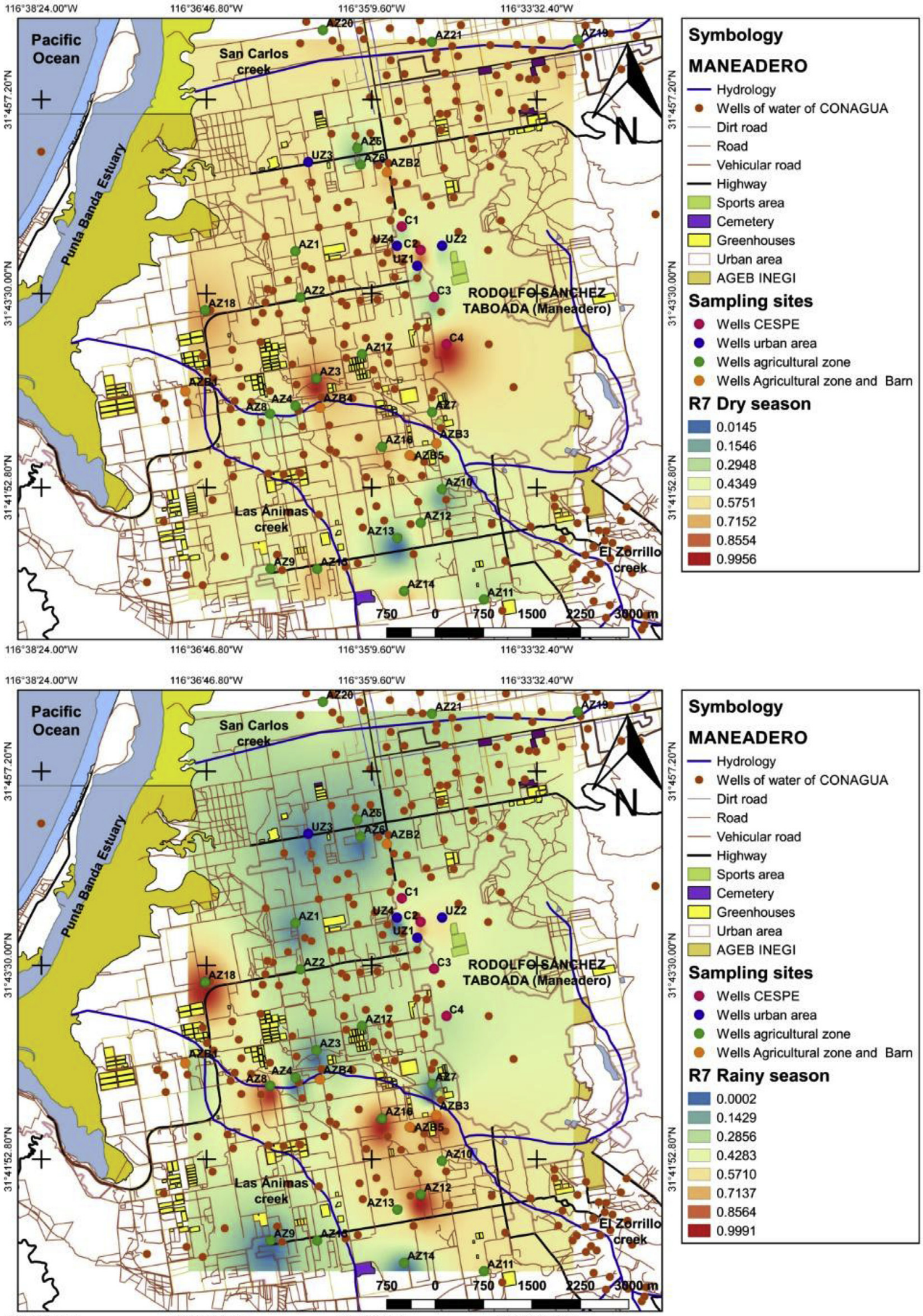

Fig. 3. Maps of fecal contamination distribution in the Valley of Maneadero, a) R7 dry season, b) R7 rainy season.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2018.10.104.

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